

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization International Bureau



(43) International Publication Date
30 September 2004 (30.09.2004)

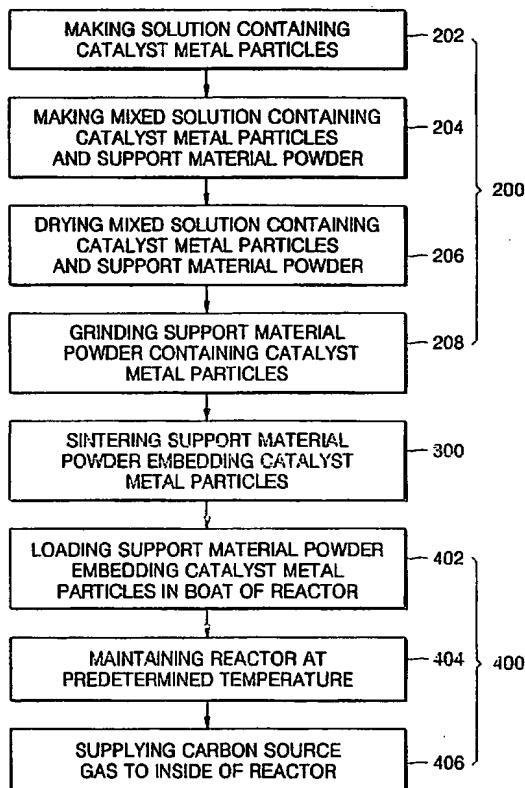
PCT

(10) International Publication Number
WO 2004/083113 A1

- (51) International Patent Classification⁷: **B82B 3/00**
- (21) International Application Number: **PCT/KR2004/000577**
- (22) International Filing Date: 17 March 2004 (17.03.2004)
- (25) Filing Language: Korean
- (26) Publication Language: English
- (30) Priority Data:
10-2003-0017616 20 March 2003 (20.03.2003) KR
10-2004-0017644 16 March 2004 (16.03.2004) KR
- (71) Applicant and
(72) Inventor: LEE, Cheol-Jin [KR/KR]; 304-1004 Hyundai 3cha Apt., Nawoon2-dong, Gunsan-city, Jeollabuk-do 573-352 (KR).
- (74) Agent: LEE, Young-Pil; The Cheonghwa Bldg., 1571-18 Seocho-dong, Seocho-gu, Seoul 137-874 (KR).
- (81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

[Continued on next page]

(54) Title: MASSIVE SYNTHESIS METHOD OF DOUBLE-WALLED CARBON NANOTUBES USING THE VAPOR PHASE GROWTH



(57) Abstract: A method of massively synthesizing double-walled carbon nanotubes is provided. In the method, catalyst metal particles having a size of a few nanometers are embedded in nano pores of a support material powder. Then, the support material powder embedding the catalyst metal particles is sintered at a temperature of 700-900°C. Then, the support material powder embedding the catalyst metal particles is loaded in a reactor. Thereafter, high purity double-walled carbon nanotubes are formed massively by vaporizing a carbon source solution at a temperature of 700-1100°C and supplying the vaporized carbon source gas, or by directly supplying a carbon source gas to the reactor.



Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

4/10/05
JC20 Rec'd PCT/PTO 20 SEP 2005

MASSIVE SYNTHESIS METHOD OF DOUBLE-WALLED CARBON NANOTUBES USING THE VAPOR PHASE GROWTH

5 Technical Field

The present invention relates to a method of synthesizing double-walled carbon nanotubes, and more particularly, to a method of massively synthesizing double-walled carbon nanotubes using a vapor phase growth.

10 Background Art

A carbon nanotube is a graphite sheet curled in a cylindrical shape. According to the number of graphite sheets, carbon naotubes are classified into single-walled carbon nanotubes having a single graphite sheet, double-walled carbon nanotubes having double graphite sheets, and multiwalled carbon nanotubes having three or more graphite sheets.

15 Since the double-walled carbon nanotube has the advantages of both the single-walled carbon and the multiwalled carbon nanotube, its various applications in an electron emission device, an electronic device, a sensor, a high strength composite material and the like are anticipated. To use the double-walled carbon nanotube, it is essentially requested to synthesize a high purity double-walled carbon nanotube inexpensively and massively.

20 As methods of synthesizing the double-walled carbon nanotube, there are an electric discharge method and a vapor phase synthesis method. When using the electric discharge method, an amorphous carbon material is generated as a by-product in addition to carbon nanotubes. Accordingly, to obtain high purity carbon nanotubes, thermal and chemical filtration is essentially required. Also, it is difficult to massively and inexpensively synthesize carbon nanotubes using the electric discharge method.

25 Due to the above difficulties, the vapor phase synthesis method is gaining popularity as an alternative to synthesize the high purity carbon nanotube inexpensively and massively. Then, when double-walled carbon nanotubes are synthesized by various vapor phase synthesis methods reported up to now, production yield of the double-walled carbon nanotube is very low, and massive single-walled nanotube and amorphous carbon particles are created together with the double-walled carbon

nanotube.

Disclosure of the Invention

The present invention provides a method of massively synthesizing high purity
5 double-walled carbon nanotubes having a diameter less than a few nanometers by a
vapor phase method.

According to an aspect of the present invention, there is provided a method of
synthesizing double-walled carbon nanotubes. In the method, catalyst metal particles
composed of Fe, Co, Ni, Mo or an alloy of these elements and having a size of 2-5 nm
10 are embedded in nano pores of a support material powder composed of MgO, Al₂O₃,
zeolite or silica.

Then, the support material powder in which the catalyst metal particles are
embedded is sintered. Thereafter, the double-walled carbon nanotubes are formed by
supplying a carbon source gas to the catalyst metal particles embedded in the support
15 material powder and reacting the carbon source gas with the catalyst metal particles.

To embed the catalyst metal particles in the nano pores of the support material
powder, a first solution including the catalyst metal particles is made. Then, the first
solution is mixed with the support material powder to form a second solution. Moisture
included in the second solution is removed. The removing of moisture is performed in
20 a vacuum oven for 15 hours at a temperature of 150 °C. Thereafter, the support
material powder including the catalyst metal particles is ground to form the support
material powder in which the catalyst metal particles are embedded.

The sintering may be performed in air atmosphere for 6 – 12 hours at a
temperature of 700 - 900 °C. The double-walled carbon nanotubes are formed by
25 loading the support material powder embedding the catalyst metal particles in a reactor,
which is maintained at a temperature of 700 – 1100 °C, vaporizing a carbon source
solution of an evaporator, and supplying the vaporized carbon gas.

According to the present invention, since the catalyst metal particles are
embedded in and fixed to nano pores of the support material powder, movement of the
30 catalyst metal particles is suppressed even at high temperature, it becomes possible to
massively synthesize double-walled carbon nanotubes having a uniform diameter.

Brief Description of the Drawings

The above and other features and advantages of the present invention will become more apparent by describing in detail exemplary embodiments thereof with reference to the attached drawings in which:

FIGS. 1 and 2 are schematic views of an apparatus of synthesizing carbon nanotubes, which is used in a method of synthesizing double-walled carbon nanotubes according to the present invention;

FIG. 3 is a flowchart illustrating a method of synthesizing double-walled carbon nanotubes according to the present invention;

FIG. 4 is a schematic view illustrating a synthesis mechanism of double-walled carbon nanotubes according to the present invention;

FIG. 5 is a SEM photograph of double-walled carbon nanotubes formed by the method of the present invention; and

FIGS. 6 and 7 are TEM photographs of double-walled carbon nanotubes formed by the method of the present invention.

15

Best mode for carrying out the Invention

The present invention will now be described more fully with reference to the accompanying drawings, in which exemplary embodiments of the invention are shown. The invention may, however, be embodied in many different forms and should not be construed as being limited to the embodiments set forth herein; rather, these 20 embodiments are provided so that this disclosure will be thorough and complete, and will fully convey the concept of the invention to those skilled in the art.

FIGS. 1 and 2 are schematic views of an apparatus of synthesizing double-walled carbon nanotubes using a method according to the present invention.

25 The double-walled carbon nanotube is synthesized using a vapor phase synthesis method.

Referring to FIGS. 1 and 2, the apparatus includes a reactor 100, a heating coil disposed outside the reactor 100, for heating the reactor 100, and a boat 104 disposed inside the reactor 100. The boat 104 is a quartz boat or a graphite boat. A catalyst 30 material where double-walled nanotubes are being grown is loaded in the boat 104. The catalyst material 106 is a powder support material containing catalyst metal particles.

The reactor 100 has a gas inlet 107 connected to an argon (Ar) gas supply

source 110 through a first gas supply pipe 108. The Ar gas supply source 110 shown in FIG. 1 is connected to a second gas supply pipe 112 for supplying Ar gas to an evaporator 119 containing a carbon source solution, for example, alcohol therein. The carbon source solution may be benzene, hexane, tetra hydrofuran (THF) or propanol.

5 The gas inlet 107 of the reactor 100 is connected to a third gas supply pipe 116 through carbon source gas is supplied. The carbon source gas is vaporized by supplying Ar gas through the second gas supply pipe 112 connected to the Ar gas supply source 110, and is then supplied to the reactor 100 through the third gas supply pipe 116.

10 In the synthesis apparatus shown in FIG. 2, the second gas supply pipe 112 is not connected to the Ar gas supply source 110 and a carbon gas supply source 118 is connected directly to the third gas supply pipe 116. Accordingly, the synthesis apparatus is supplied carbon source gas through the third gas supply pipe 116 connected to the carbon gas supply source 118.

15 The carbon source gas supplied from the carbon gas supply source 118 is, for example, acetylene, methane, ethylene, propane, CO or the like. Both the supply methods of carbon gas shown in FIGS. 1 and 2 can be used and do not cause any trouble in synthesizing the double-walled carbon nanotubes of the present invention.

20 A first valve 120, a second valve 122 and a third valve 124 are installed on the first gas supply pipe 108, the second gas supply pipe 112 and the third gas supply pipe 116, respectively so as to block the gas supply to the reactor 100. The gases introduced through the inlet 107 of the reactor 100 are moved in a direction indicated by an arrow and is then exhausted through a gas outlet 126.

25 In the synthesis apparatus of the double-walled carbon nanotubes using the vapor phase synthesis method, carbon source gas is supplied through the evaporator 119 while the reactor is kept in a contact temperature, or carbon source gas is supplied to the reactor 100, and then the double-walled carbon nanotubes are grown by the catalyst material 106 using the vapor phase synthesis method. When growing the double-walled carbon nanotubes, Ar gas is supplied through 110 if necessary.

30 FIG. 3 is a flowchart illustrating a method of synthesizing double-walled carbon nanotubes according to the present invention, and FIG. 4 is a schematic view illustrating a synthesis mechanism of double-walled carbon nanotubes according to the present invention.

Specifically, to synthesize the double-walled carbon nanotubes, it is essentially required to form catalyst metal particles having proper sizes and to supply proper carbon source gas necessary. To form the catalyst metal particles with proper sizes, it is necessary to select a support material having a size of a few nanometers and to adjust a concentration of the catalyst metal particles in a solution in which the catalyst metal particles are dissolved. Finally, the carbon source gas reacting with the catalyst metal particles should be properly supplied. At this time, a synthesis temperature acts as an important factor.

The method of synthesizing double-walled carbon nanotubes according to the present invention includes three operations. In the first operation (operation 200), catalyst metal particles composed of Fe, Co, Ni, Mo or an alloy of the aforementioned metal elements and having a size of 2 – 5 nm are embedded in nano pores of a support material in powder form composed of MgO, Al₂O₃, zeolite or silica.

The operation 200 will now be described in more detail.

First, a solution containing catalyst metal particles is fabricated. (Operation 202) The solution containing catalyst metal particles is, for example, Fe(NO₃)₃·9H₂O, FeCl₂·9H₂O, CoSO₄·XH₂O, Co(NO₃)₂·6H₂O, Ni(NO₃)₂·6H₂O, NiSO₄·6H₂O or the like. A solution containing the catalyst metal particles composed of Mo is prepared by diluting MoS₂, MoCl₂ or the like in deionized water, or by diluting solid Mo in deionized water. Thus, the solution containing catalyst metal particles is made by mixing the aforementioned materials and then diluting the mixed materials in deionized water for 1 hour.

Next, the solution containing catalyst metal particles is mixed with the mixed solution of the deionized water and the support material (i.e., support material powder) in an ultrasonic apparatus for 1 hour, thereby fabricating a mixed solution (operation 204).

If the mixed solution containing the catalyst metal particles and the support material powder is a solution containing Fe, Ni or Co, Mo, and MgO, a molar ratio of Fe, Ni or Co : Mo : MgO is 0.7 – 1 : 0.1 – 0.3 : 10 – 13. If the mixed solution containing the catalyst metal particles and the support material powder is a solution containing Fe or Ni, Mo, and MgO, a molar ratio of Fe : Ni : Mo : MgO is 0.7 – 1 : 0.1 – 0.3 : 0.1 – 0.3 : 10 – 13. If the mixed solution containing the catalyst metal particles and the support material powder is a solution containing Fe or Co, Mo, and MgO, a molar ratio of Fe :

Co : Mo : MgO is 0.7 – 1 : 0.1 – 0.3 : 0.1 – 0.3 : 10 – 13.

Next, the mixed solution containing the catalyst metal particles and the support material powder is unloaded from the ultrasonic apparatus and is then dried in a vacuum oven for 15 hours at a temperature of 150 °C to remove moisture (operation 206). Thereafter, to further miniaturize the support material powder, which moisture is removed from and contains the catalyst metal particles, the support material powder is ground and pulverized in a mortar, and the catalyst metal particles are embedded in the pores of the pulverized support material powder (operation 208).

Meanwhile, in the second operation of the synthesis method according to the present invention, the support material powder embedding the catalyst metal particles in the pores thereof is sintered (operation 300). Since the sintering increases the surface area of the support material powder, it is possible to increase density of the catalyst metal particles substantially participating in a reaction during the synthesis of the double-walled carbon nanotubes.

Due to the sintering of the support material powder embedding the catalyst metal particles, since the catalyst metal particles can be properly adjusted in a size of 2 – 5 nm and are activated, it is possible to greatly increase the yield of the carbon nanotubes when synthesizing the carbon nanotubes.

During the sintering, the support material powder embedding the catalyst metal particles is loaded in a furnace and is sintered in air atmosphere for 6 – 12 hours at a temperature of 700 - 900 °C. The sintering temperature and time can be adjusted, and hydrogen or argon gas may be used as an atmosphere gas.

In the third operation of the synthesis method according to the present invention, as carbon source gas is supplied to the catalyst metal particles embedded on the support material, a catalyst reaction between the carbon source gas and the catalyst metal particles occurs, so that the double-walled nanotubes are formed (operation 400).

The forming of the double-walled carbon nanotubes will now be described in more detail with reference to FIGS. 1 through 4. First, the support material 106 embedding the catalyst metal particles is provided in the boat 104, and the boat 104 is loaded in the reactor 100 (operation 402).

Next, 1000 sccm of argon gas is supplied to the reactor 100 while maintaining the reactor 100 at a predetermined temperature, for example, at a temperature of 700 – 1100 °C. (operation 404)

Next, when the synthesis apparatus of FIG. 1 is used, the supply of argon gas to the reactor 100 is stopped, and 1000 sccm of argon gas is supplied to the evaporator 119 for 10 minutes, thereby vaporizing carbon source solution, for example, alcohol, and vaporized carbon source gas is supplied through the third gas supply pipe 116.

5 The flow rate of the argon gas supplied to the evaporator 119 can be adjusted according to a size of the reactor 100. In addition to alcohol, the carbon source solution may be benzene, hexane, tetra hydrofuran (THF), propanol or the like.

Meanwhile, when the synthesis apparatus of FIG. 2 is used, the supply of argon gas to the reactor 100 is stopped, and carbon source gas, for example, acetylene is supplied in a flow rate of 40 sccm through the third gas supply pipe 116 for 20 minutes. 10 In addition to acetylene, the carbon source gas may be methane, propane, or CO. Accordingly, by the carbon source gas supplied to the reactor 100, a catalyst reaction occurs at the catalyst metal particles, so that the double-walled carbon nanotubes are synthesized (operation 406).

15 It is preferable that the reactor 100 is maintained at atmospheric state during the synthesis of the double-walled carbon nanotubes. After the synthesis of the double-walled carbon nanotubes is completed, the temperature of the reactor is gradually lowered while supplying argon gas in a flow rate of 500 sccm to the reactor 100.

20 In the synthesis of the double-walled carbon nanotubes, the flow rate of argon gas supplied to the evaporator 119 is properly adjusted, or the flow rate of carbon source gas directly supplied to the reactor 100 is properly adjusted. Accordingly, it is suppressed that excessive carbon elements are supplied on a surface of the catalyst metal particles, amorphous carbon material adsorbed on the surface of the catalyst 25 metal particles is removed, or it is suppressed that amorphous carbon clod or carbon particle is attached on an outer wall of the growing carbon nanotubes.

The synthesis (growth) mechanism of the double-walled carbon nanotubes on the catalyst metal particles will now be described in more detail with reference to FIGS. 1, 2 and 4.

30 The catalyst metal particles 505 are embedded in and fixed to nano pores 503 of the support material powder 501. When carbon source gas (ex. R-OH where R represents hydrocarbon) is supplied to the reactor 100 into which the support material powder embedding the catalyst metal particles in the nano cores 503 thereof is loaded,

the supplied carbon source gas is pyrolyzed in vapor phase, thereby forming carbon units (C=C or C) and free hydrogen (H₂). Also, after the carbon units are adsorbed on surfaces of the catalyst metal particles 505, they are diffused inwardly and dissolved. As the carbon units diffused into an inside of the catalyst metal particles 505 are 5 accumulated, double-walled carbon nanotube starts to grow. If the carbon units are continuously supplied, the double-walled carbon nanotube 507 continues to grow from the catalyst metal particles by a catalyst action (reaction).

Since the catalyst metal particles 505 are embedded in and fixed to the nano pores 503 of the support material powder 501, movement of the catalyst metal particles 10 505 is suppressed even in a high temperature required for the synthesis of the carbon nanotubes, and accordingly it becomes possible to synthesize the double-walled carbon nanotubes having a uniform diameter.

Also, since the carbon nanotubes are synthesized on the catalyst metal particles supported in and fixed to the nano pores in an optimum carbon source supply condition, 15 amorphous carbon clods are not formed and a high purity carbon nanotubes can be formed. Hence, the invention does not need a filtering operation after the synthesis of the carbon nanotubes.

FIG. 5 is a SEM photograph of double-walled carbon nanotubes formed by the method of the present invention, and FIGS. 6 and 7 are TEM photographs of 20 double-walled carbon nanotubes formed by the method of the present invention.

Specifically, the carbon nanotubes shown in FIG. 5 are samples not subjected to a filtering operation. As shown in FIG. 5, it is understood that massive carbon tubes are synthesized without defects such as amorphous carbon clods. Also, the carbon nanotubes shown in FIG. 5 have a diameter of 20-40 nm. In addition, the TEM 25 photographs of FIGS. 5 and 6 show that the double-walled carbon nanotubes are formed.

As described above, according to the present invention, since the catalyst metal particles are embedded in and fixed to nano pores of the support material powder, movement of the catalyst metal particles is suppressed even in a high temperature, it 30 becomes possible to synthesize double-walled carbon nanotubes having a uniform diameter.

Also, the present invention makes it possible to properly control the size of the catalyst metal particles at 2-5 nm and to activate the catalyst metal particles.

Accordingly, since amorphous carbon clods are not formed, high purity carbon nanotubes can be formed and production yield of the carbon nanotubes can be enhanced.

Further, since amorphous carbon clods are not formed, the synthesis method of 5 the present invention does not need a filtering operation after the synthesis of the carbon nanotubes. Furthermore, high purity double-walled carbon nanotubes can be synthesized massively by a simple method without using a complicated apparatus or a subsequent filtering operation.

10 Industrial Applicability

The method of synthesizing the double-walled carbon nanotube according to the present invention can be employed, for example, in an electron emission device, an electronic device, a sensor, a high strength composite material, and the like.

What is claimed is:

1. A method of synthesizing double-walled carbon nanotubes, the method comprising:

embedding catalyst metal particles composed of Fe, Co, Ni, Mo or an alloy of the elements and having a size of 2-5 nm in nano pores of a support material powder composed of MgO, Al₂O₃, zeolite or silica;

sintering the support material powder in which the catalyst metal particles are embedded; and

10 forming the double-walled carbon nanotubes by supplying a carbon source gas to the catalyst metal particles embedded in the support material powder and reacting the carbon source gas with the catalyst metal particles.

2. The method of claim 1, wherein the embedding the catalyst metal particles in the nano pores of the support material powder comprises:

15 making a first solution including the catalyst metal particles;

mixing the first solution with the support material powder to form a second solution;

removing moisture included in the second solution; and

20 pulverizing the support material powder including the catalyst metal particles to form the support material powder in which the catalyst metal particles are supported.

3. The method of claim 2, wherein the removing the moisture is performed by a vacuum oven for 15 hours at a temperature of 150 °C.

25 4. The method of claim 2, wherein if the second solution is a solution containing Fe, Ni or Co, Mo, and MgO, a molar ratio of Fe, Ni or Co : Mo : MgO is 0.7-1 : 0.1-0.3 : 10-13,

if the second solution is a solution containing Fe or Ni, Mo, and MgO, a molar ratio of Fe : Ni : Mo : MgO is 0.7-1 : 0.1-0.3 : 0.1-0.3 : 10-13, and

30 if the second solution is a solution containing Fe or Co, Mo, and MgO, a molar ratio of Fe : Co : Mo : MgO is 0.7-1 : 0.1-0.3 : 0.1-0.3 : 10-13.

5. The method of claim 1, wherein the sintering is performed in air atmosphere for 6-12 hours at a temperature of 700 - 900 °C.

6. The method of claim 1, wherein the forming the double-walled carbon nanotubes comprises:

loading the support material powder embedding the catalyst metal particles in a reactor;

maintaining the temperature of the reactor including the support material powder at 700-1100 °C; and

10 supplying a carbon source solution selected from the group consisting of alcohol, benzene, hexane, THF (tetra hydrofuran) and propanol, to an inside of the reactor in a gas form using an evaporator.

7. The method of claim 1, wherein the forming the double-walled carbon nanotubes comprises:

loading the support material powder embedding the catalyst metal particles in a reactor;

maintaining the temperature of the reactor including the support material powder at 700-1100 °C; and

20 supplying a carbon source gas selected from the group consisting of acetylene, methane, ethylene, propane and CO to an inside of the reactor.

1/4

FIG. 1

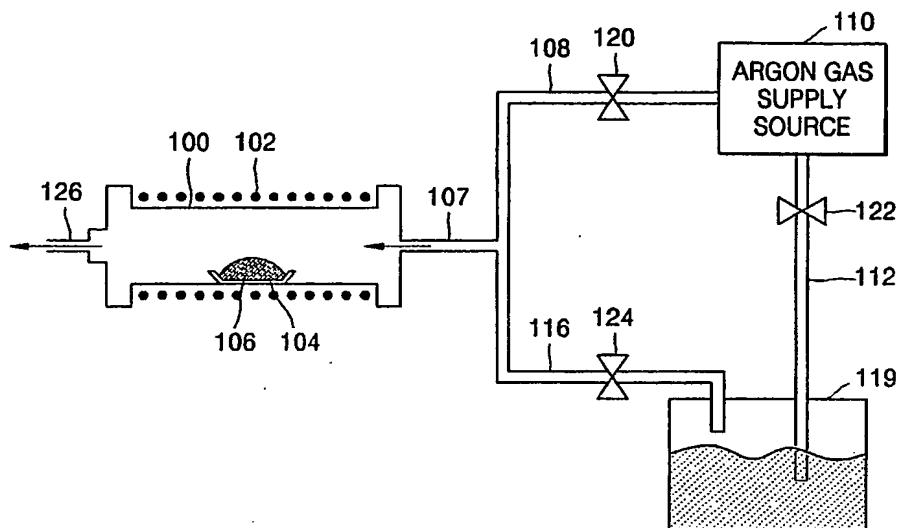
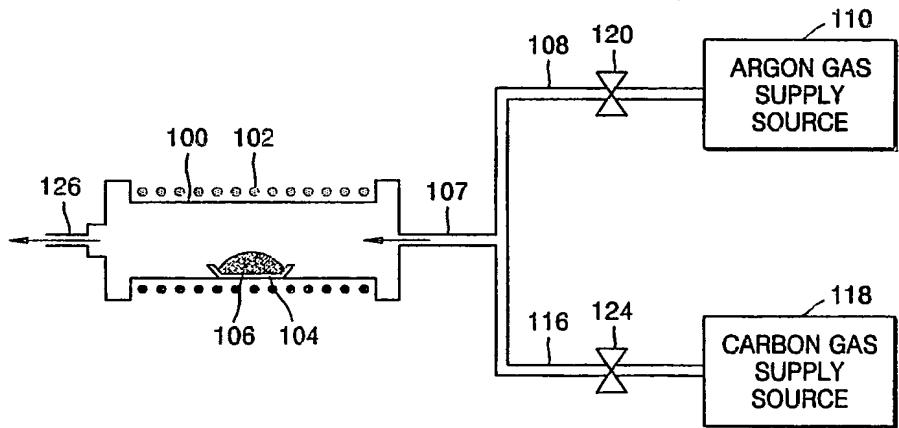
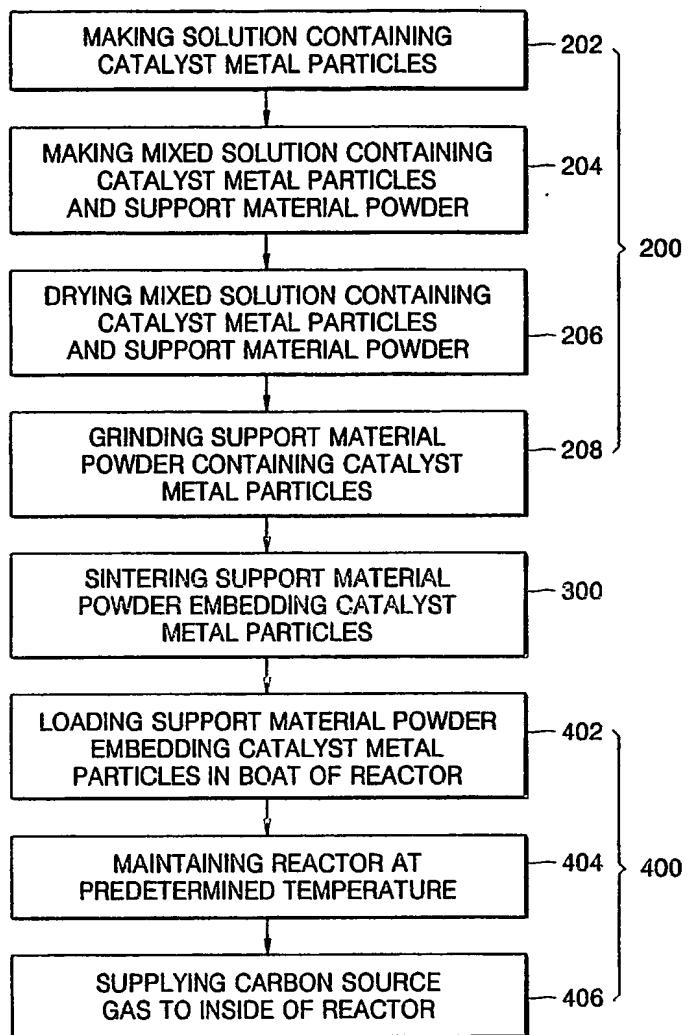


FIG. 2



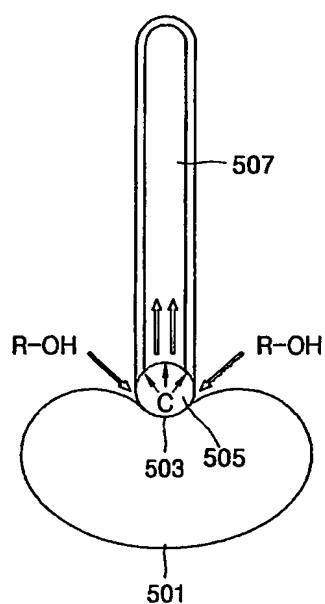
2/4

FIG. 3

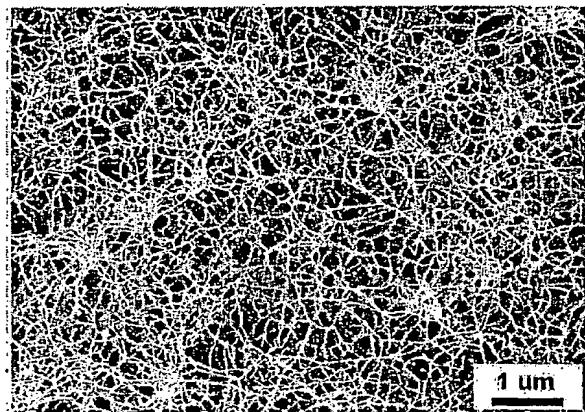


3/4

FIG. 4



4/4
FIG. 5

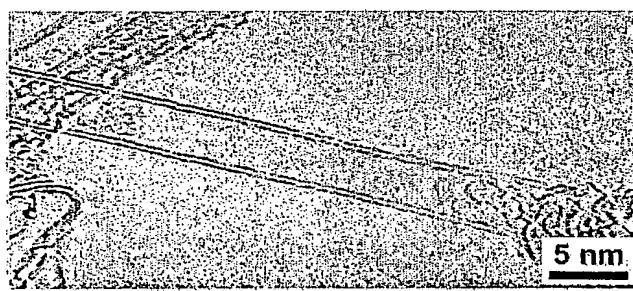


DEC 1 2004 BY UHRY

FIG. 6



FIG. 7



INTERNATIONAL SEARCH REPORT

International application No.

PCT/KR2004/000577

A. CLASSIFICATION OF SUBJECT MATTER**IPC7 B82B 3/00**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7 B82B 3/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
KIPASS, USP, PAJ "carbon nanotube, metallic catalyst, chemical vapor deposition, zeolite, alumina"**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2002/165091 A1 (Daniel E. Resasco) 07. Nov. 2002 See abstract, column2 [0014]-[0019] and column2 [0031]-[0056]	1-7
Y	JP 2001-20071 A (Lee Cheol Jin , Iljin Nanotech Co., Ltd.) 23. Jan. 2001 See abstract and claims1-15	1-7
A	EP 1,061,043 A1 (Lee Cheol Jin, Iljin Nanotech Co., Ltd.) 20. Dec. 2000 See the whole document	1-7
A	JP 2002-29718 A (Hatanaka Takeshi) 29. Jan. 2002 See the whole document	1-7
A	JP 2002-293524 A (OSAKA GAS CO LTD) 29. Jan. 2002 See the whole document	1-7

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family
--	--

Date of the actual completion of the international search

09 JULY 2004 (09.07.2004)

Date of mailing of the international search report

12 JULY 2004 (12.07.2004)

Name and mailing address of the ISA/KR

Korean Intellectual Property Office
920 Dunsan-dong, Seo-gu, Daejeon 302-701,
Republic of Korea

Facsimile No. 82-42-472-7140

Authorized officer

JWA, Seung Kwan

Telephone No. 82-42-481-5560



INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.

PCT/KR2004/000577

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 2002/165091 A1	07.11.2002	NONE	
JP 2001-20071 A	23.01.2001	US 6350488 BA JP 3442032 B2 CN 1277145 A	26.02.2002 02.09.2003 20.12.2000
EP 1,061,043 A1	20.12.2000	EP 1061043 A1 JP 3442033 B2 CN 1277147 A	20.12.2000 02.09.2003 20.12.2000
JP 2002-29718 A	29.01.2002	NONE	
JP 2002-293524 A	29.01.2002	NONE	